JVSTB
JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY B

Influence of solubility switching mechanism on resist performance in molecular glass resists

Richard A. Lawson, Cheng-Tsung Lee, Clifford L. Henderson, Robert Whetsell, Laren Tolbert et al.

Citation: J. Vac. Sci. Technol. B **25**, 2140 (2007); doi: 10.1116/1.2801885
View online: http://dx.doi.org/10.1116/1.2801885
View Table of Contents: http://avspublications.org/resource/1/JVTBD9/v25/i6
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Influence of solubility switching mechanism on resist performance in molecular glass resists

Richard A. Lawson, Cheng-Tsung Lee, and Clifford L. Henderson[a)]
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Robert Whetsell and Laren Tolbert
School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Wang Yueh
Intel Corporation, Portland, Oregon 97124

(Received 11 June 2007; accepted 1 October 2007; published 7 December 2007)

Five different molecular glass chemically amplified photoresists which utilized different solubility switching mechanisms and chemistries, based on a tris(4-hydroxyphenyl)ethane (THPE) core, were synthesized and their performance compared. Three different positive tone systems were designed based on acid catalyzed deprotection of a phenolic hydroxyl group protected with one of the following groups: tert-butoxycarbonyl (tBoc), tetrahydropyranyl, or ethoxyethyl. Two negative tone systems were designed; one using cationic epoxide polymerization of pendant epoxides and one using condensation of the unprotected THPE with a multifunctional cross-linking additive. The tBoc system and negative tone systems showed good performance under deep UV and large field e-beam patterning, but the epoxide system showed far superior performance for high resolution electron beam patterning. It was able to produce 50 nm 1:1 line/space patterns and 30 nm lines on 1:3 line/space patterns with high sensitivity, good contrast, and a very low line edge roughness (3σ) of 2.3 nm using 100 keV electron beam patterning.
[DOI: 10.1116/1.2801885]

I. INTRODUCTION

In recent years, molecular glass photoresists have received significant attention as potential replacements for polymer based photoresists in sub-65 nm advanced lithography.[1–3] Among the perceived advantages of molecular resists over polymers are the following: (1) they can be repeatedly synthesized with precise molecular weight, compositional, and stereochemical control, and (2) their much smaller molecular size and consistent molecular composition should improve dissolution inhomogeneity which can reduce line edge roughness (LER). Molecular resists have been shown, both in simulation and experiment, to provide improvements in LER compared to polymer resists.[4–6] Although molecular glass materials may offer many potential advantages over polymeric chemically amplified resists (CARs), there are still many things that are unknown about this class of materials that could potentially cause problems. Removal and subsequent volatilization of protecting groups in positive tone molecular resists can cause a loss of up to approximately 50% of the mass of the resist, possibly leading to a loss of pattern quality. The small sizes of molecular resist compounds, and often correspondingly low glass transition temperatures, can also lead to problems such as more significant photoacid diffusion and reduced mechanical strength and integrity. Characterizing and overcoming these problems may be the key to the widespread acceptance of molecular glass resists.

A variety of solubility switching mechanisms have been proposed and used for molecular resists.[7,8] These include positive tone chemically amplified compositions with several different types of protecting groups based on phenol deprotections[9] and carboxylic acid deprotections.[10] A few different negative tone materials have also been used, based on either epoxide ring opening cross-linking[11] or hydroxyl cross-linking via an additional additive.[12] Although many solubility switching mechanisms have been used, they have been investigated on many different molecular cores in such a way that no direct comparison of the advantages and disadvantages of each solubility switching scheme could be directly made on a common molecular core platform. In addition, it would appear that the majority of previous publications report only the positive aspects of their results, while not discussing in any detail the negative features and results from the materials investigated. This study compares different solubility switching mechanisms in molecular resists, all based on a common core molecule, revealing both the advantages and disadvantages of each mechanism.

The common core molecule used in this study is one of the smallest cores that will form amorphous glasses, 1,1,1-tris(4-hydroxyphenyl)ethane (THPE). In total, five different chemically amplified resists were formulated based on this common core. Three positive tone resists were made, one a high activation energy resist, 1,1,1-tris(4-*tert*-

[a)]Author to whom correspondence should be addressed; electronic mail: cliff.henderson@chbe.gatech.edu

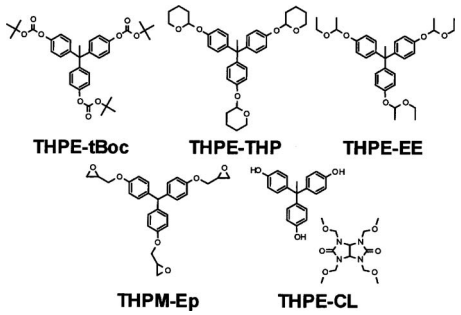

FIG. 1. Chemical structures of the five molecular glass resists used in this work.

butoxycarbonyloxyphenyl)ethane (THPE-tBoc), and two low activation energy resists, 1,1,1-tris(4-tetrahydropyranyloxyphenyl)ethane (THPE-THP) and 1,1,1-tris(4-ethoxyethoxyphenyl)ethane (THPE-EE). One negative tone resist, tris(4-(oxiran-2-ylmethoxy)phenyl)methane (THPM-Ep), is based on epoxide ring opening cationic polymerization where the multifunctional core cross-links. The other negative tone resist (THPE-CL) was made by blending the THPE core with both a photoacid generator and an additional cross-linking agent, 1,3,4,6-tetrakis(methoxymethyl)glycoluril. This cross-linking agent reacts with the phenolic hydroxy functionality of THPE in the presence of acid to produce a cross-linked material.[13] Figure 1 shows the structure of each of the cores in this resist.

II. EXPERIMENT

A. Materials and equipment

THPE, 1,3,4,6-tetrakis(methoxymethyl)glycoluril, and 2,3-dihydropyran were purchased from TCI America. THPM-Ep, ethyl vinyl ether, propylene glycol methyl ether acetate (PGMEA), methyl isobutyl ketone (MIBK), hexamethydisilazane (HMDS), and triphenylsulfonium nonaflate (TPS-Nf) were purchased from Sigma-Aldrich. TPS-SbF_6 was purchased from Midori Kagaku Co., Ltd. AZ300 tetramethylammonium hydroxide (TMAH) developer was donated by AZ Electronic Materials. THPE-tBoc was synthesized as previously reported.[14] Deep ultraviolet (DUV) contrast curves were made using Oriel Instruments 500W Hg–Xe arc lamp with a 248 nm bandpass filter with film thicknesses measured using a M-2000 spectroscopic ellipsometer (J.A. Woolam, Inc.) over the wavelengths of 350–1000 nm using a Cauchy layer to model the resist film. Electron beam lithography was done using a JEOL JBX-9300FS electron-beam lithography system with 100 keV acceleration voltage, 2 nA current, and 10 nm single-pixel shot pitch. Resolution tests were done on 75 nm thick films coated onto a 46 nm thick silicon nitride membrane windows.[15] Further details about DUV and e-beam lithography procedures can be found elsewhere.[14]

B. Synthesis

1. 1,1,1-tris(4-tetrahydropyranyloxyphenyl)ethane (THPE-THP)

2.53 g (8.26 mmol) of 1,1,1-tris(4-hydroxyphenyl)ethane was dissolved in 20 ml of ethyl acetate in a round bottom flask. 8 mL of 2,3-dihydropyran and eight drops of trifluoroacetic acid were added to the mixture. After stirring overnight, a white precipitate had formed in the flask. This precipitate was collected by filtration and dissolved in 20 ml of dichloromethane to which was added 8 ml of 2,3-dihydropyran and six drops of trifluoroacetic acid. After stirring for two days, 20 ml of 0.261*N* TMAH was added; the organic phase was extracted, washed with water (20 ml) twice, and dried with $MgSO_4$. The solvent was removed *in vacuo* to yield 2.82 g of THPE-THP as a white powder. Yield: 77%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 1.5–2.0 (18H), 2.09 (3H), 3.60 (3H), 3.92 (3H), 5.37 (3H), 6.91 (6H), 6.98 (6H).

2. 1,1,1-tris(4-ethoxyethoxyphenyl)ethane (THPE-EE)

THPE-EE was synthesized analogously using to THPE-THP using ethyl vinyl ether instead of dihydropyran. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm) 1.21 (*t*, 9H), 1.48 (*d*, 9H), 3.55 (*m*, 3H), 3.80 (*m*, 3H), 5.35 (3H), 6.87 (6H), 6.98 (6H).

C. Resist processing

Due to the unique nature of each resist, they each received slightly different processing conditions as described below. THPE-tBoc and THPE-THP were dissolved in cyclohexanone along with 5 mol % TPS-Nf (with respect to the functionalized THPE solids), spin cast into films, and postapply baked at 90 °C for 2 min to form 100 nm thick films. Postexposure, these films received a postexposure bake (PEB) at 90 °C for 60 s and were developed in 0.065*N* TMAH (1/4 dilution of AZ300 MIF) for 30 s. THPE-EE was an oil at room temperature, and so no further lithographic testing was performed on that material. THPM-Ep was dissolved in PGMEA along with 5 mol % TPS-SbF_6 (with respect to the THPM-Ep solids), spin cast into films, and soft baked at 60 °C for 4 min to form 120 nm thick films. The THPM-Ep films received a PEB at either 60 or 90 °C for 60 s and were developed in MIBK for 30 s followed by an isopropanol rinse. The THPE-CL resist was formulated by dissolving THPE into PGMEA along with 15 wt % (relative to THPE solids) of 1,3,4,6-tetrakis(methoxymethyl)glycoluril and 5 mol % (relative to THPE solids) TPS-Nf as a photoacid generator (PAG). THPE-CL films were soft baked at 90 °C for 2 min to form 100 nm thick films. The PEB for the THPE-CL films was 90 or 110 °C for 60 s, followed by development in 0.013*N* TMAH (1/20 dilution of AZ300 MIF) for 30 s. All solutions were filtered through 0.2 μm PTFE filters before use. No base quencher was used in these resist formulations so as to prevent any effect on LER and to eliminate any interaction or segregation effects of base with the various different resists.

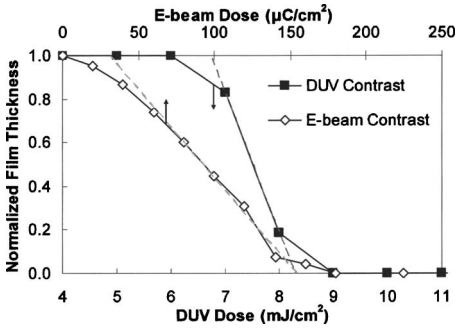

FIG. 2. Contrast curves of THPE-tBoc under DUV and e-beam (100 keV) exposures.

III. RESULTS AND DISCUSSION

A. THPE-tBoc

THPE-tBoc behaves much like its polymeric analog, tBoc protected poly(hydroxystyrene) (tBoc-PHOST). It was thermally stable to approximately 130–140 °C, when the tBoc groups began to thermally deprotect, and it could be developed in 0.261*N* TMAH with no appreciable dark loss. It could be processed without addition of primer, but performed better in developer when HMDS was used to prime the silicon substrate before coating. It exhibited film thickness loss in the exposed areas during PEB of upwards of 50% of the total thickness due to volatilization of the tBoc deprotection products.

The imaging performance of THPE-tBoc under DUV exposure was rather good. Figure 2 shows the contrast curves for THPE-tBoc under DUV and e-beam exposures. Its sensitivity was approximately 8 mJ/cm^2, depending on development conditions. The contrast was also good in 0.261*N* TMAH, at approximately 8.5, but could be improved even further to 11 by using a more dilute developer of 0.065*N* TMAH. Under electron beam exposure, THPE-tBoc showed much poorer behavior. The contrast was reduced to 1.4 and the dose to clear was an unexpectedly high 153 $\mu C/cm^2$. For high resolution imaging under e-beam, no features of 100 nm or smaller could be imaged due to high levels of photoacid diffusion which blurred out smaller features. Although a PEB of 90 °C is not extremely high, photoacid diffusion is a major issue in this resist because of the high concentration of acid required to image (as judged by the dose). It is also likely that the high level of protection of the resist contributes to the reduced sensitivity under e-beam.

B. THPE-THP and THPE-EE

THPE-THP had several problems. It did not consistently form good films, even when HMDS was used to prime the silicon substrate surface. Since adhesion was poor, when the developed film was rinsed in water after exposure, large sections of the unexposed resist would lift off of the substrate. The most significant problem, however, with the use of THP as a protecting group for a resist molecule as small as THPE is that the number of protecting groups per core molecule is large, i.e., a 3:1 molar ratio in this case. The high level of THP protection is a serious problem because the dihydropyran and other deprotection products are insoluble in developer and even more significantly, the dihydropyran tends to polymerize in the presence of photoacid to form insoluble polymer films.[16,17]

In an attempt to circumvent some of the problems with the dihydropyran deprotection product of THPE-THP, THPE-EE was synthesized in the hope that the deprotection product could more easily be volatilized and would not be as reactive toward polymerization as the dihydropyran produced from the THPE-THP. Unfortunately, synthesis of the THPE-EE showed that it was an oil at room temperature. This is likely due to the presence of the flexible ether linkages in the protecting group. THPE-THP is a solid because the cyclic structure of the protecting group reduces the flexibility in the molecule relative to THPE-EE. Therefore, no further processing of the THPE-EE was attempted.

C. THPE-CL

THPE-CL had several problems even before high resolution imaging was attempted. One problem is that for a PEB of 90 °C or less, very dilute developer ($<0.026N$) must be used. This is because the THPE-CL still forms a phenolic, hydroxy terminated, low molecular weight polymer that can dissolve in sufficiently strong aqueous alkaline developers even though some cross-linking occurs. Another problem was that for a PEB of 90 °C, the developed film at maximum dose and thickness was only approximately 50% as thick as the original film. This puts the lower temperature limit for PEB processing of the THPE-CL material at 90 °C or above, which prevents the use of low temperature PEB processing that could be used to help overcome photoacid diffusion blurring.

Under DUV exposures, THPE-CL did exhibit a very high sensitivity. The D_{50} (dose to obtain 50% of maximum film thickness) for THPE-CL was on the order of 1 mJ/cm^2. However, the contrast ratio was a disappointingly low value of approximately 2 for a 90 °C PEB. Under e-beam exposure, the high sensitivity was maintained, with a D_{50} of 28 $\mu C/cm^2$ at an acceleration voltage of 100 keV. However, high resolution testing of THPE-CL using e-beam exposures revealed even more problems. For PEB temperatures less than 110 °C, all small patterns produced using e-beam patterning washed off of the substrate. Furthermore, even at the lowest PEB temperature to successfully produce viable patterns of 110 °C and at the low exposure doses (approximately at the D_{50} dose), photoacid diffusion induced pattern blur was a significant problem. No sub-100 nm patterns could be resolved, even for relaxed 1:3 pattern spacings. Any future use of THPE-CL would require significant base quencher loading and photoacid diffusion control to obtain reasonable imaging control, and the use of extremely dilute developers can be problematic due to problems in controlling and maintaining a constant developer strength.

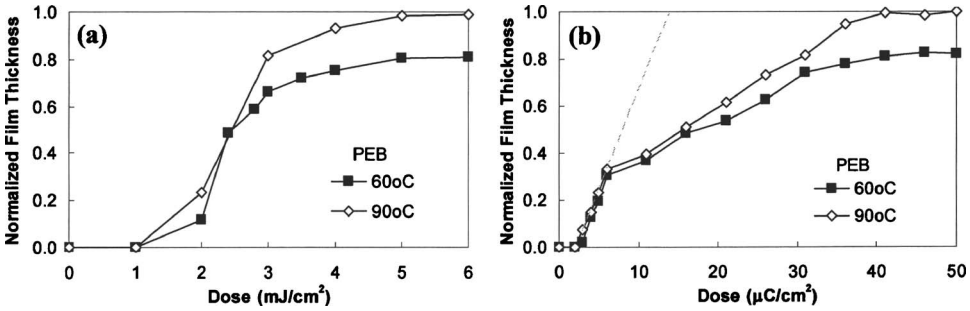

FIG. 3. Contrast curves for THPM-Ep under (a) DUV and (b) e-beam (100 keV).

D. THPM-Ep

THPM-Ep had to be preapply baked at 60 °C or less because at higher temperatures the film dewets from the silicon substrate forming defects in the film. This occurs because the terminating glycidyl ethers on THPM-Ep are so flexible that they significantly lower the melting point as compared to the unprotected compound. After exposure, the film could be postexposure baked at temperatures higher than 60 °C because the cross-linked film was much more robust. One disadvantage of using the cationic ring opening of glycidyl epoxides as a solubility changing mechanism is that this greatly limits the choice of PAGs that can be used in formulating the chemically amplified resist. Only non-nucleophilic acid counterions can be used; sulfonic acids, including perfluorinated sulfonic acids, will not effectively cause polymerization.[18] Unfortunately, most non-nucleophilic acids such as hexafluoroantimonate are unfavorable for use in semiconductor applications for a variety of reasons.

Despite these drawbacks, THPM-Ep has many good properties. Unlike positive tone resists, it exhibited no change in film thickness or shrinkage upon PEB. Multiple different solvents can be used for development including MIBK, THF, and PGMEA. Choice of developer could have an effect on LER due to differences in swelling and pattern collapse, but was not investigated in this study; MIBK was used as developer for all results shown for THPM-Ep. However, use of a solvent for development is generally considered less favorable for semiconductor processing as compared to aqueous based developers. THPM-Ep imaged under DUV with good sensitivity, reaching around 75% of its maximum thickness at an exposure dose of only 3 mJ/cm^2. It also had reasonable contrast, with a contrast ratio of approximately 5. Figure 3 shows DUV and e-beam contrast curves for THPM-Ep for different PEB conditions. In e-beam, THPM-Ep still shows excellent sensitivity with a D_{50} of 16 $\mu C/cm^2$. Interestingly, there appears to be a potentially more favorable imaging dose of approximately 6–8 $\mu C/cm^2$ which gives only 33% of the maximum film thickness but at the highest contrast of approximately 2.5. It can be seen that PEB temperatures from 60 to 90 °C can be used with little loss in performance, the only major differences being that at 90 °C the final film thickness is the same as before development, while at 60 °C, there is still around 20% dark loss even at high doses.

THPM-Ep showed excellent high resolution imaging. Figure 4 shows 80 nm 1:1 line/space patterns for THPM-Ep with a PEB of 60 °C (THPM-Ep-60), and 50 nm 1:1 line/space and 30 nm 1:3 line/space patterns for THPM-Ep with a PEB of 90 °C (THPM-Ep-90). THPM-Ep-90 resolved 1:1 patterns down to 50 nm and 1:3 patterns down to 30 nm, while THPM-Ep-60 gave excellent 1:1 patterns down to 55 nm and 1:3 patterns down to 40 nm. Failure at smaller pitch sizes was not due to image blurring, but was instead due simply to pattern collapse as the aspect ratio of features increased due to the pattern size decreasing at constant film thickness. It is believed that THPM-Ep-90 gave smaller features than THPM-Ep-60 because of the more complete cross-linking which occurs at the higher PEB temperature, thus generating more robust features. No major difference between the two PEB conditions due to photoacid diffusion could be easily observed, but was likely due to lack of any identical comparable lines smaller than 40 nm.

Using the 80 nm 1:1 line/space patterns, the LER and linewidth roughness (LWR) were calculated. For THPM-Ep-60, LER (3σ) was 2.7 nm and LWR (3σ) was 3.8 nm, while for THPM-Ep-90, an even smaller LER (3σ) of 2.3 nm and LWR (3σ) of 3.4 nm were obtained. These are very low

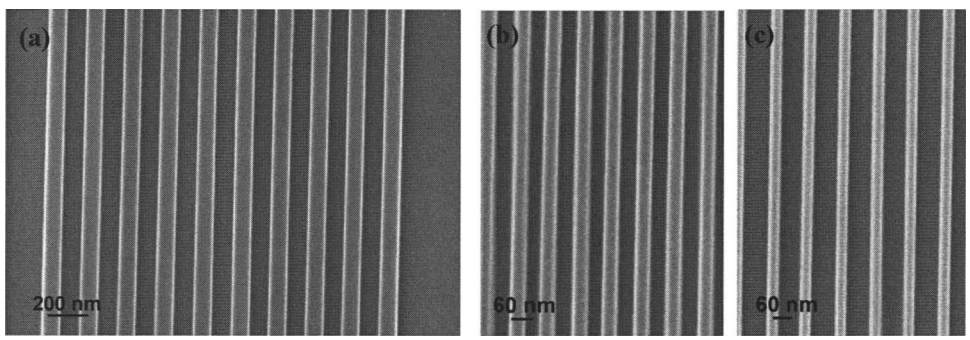

FIG. 4. SEM of e-beam patterning of (a) THPM-Ep-60 80 nm 1:1 line/space, (b) THPM-Ep-90 50 nm 1:1 line/space, and (c) THPM-Ep-90 30 nm 1:3 line/space.

values for LER, much lower than the 5 nm minimum that is commonly reported for conventional CARs.[19] This 5 nm limit appears to hold true for both polymeric and molecular glass resists. The excellent LER performance of this resist can likely be attributed to several things. The film should be very uniform in that each individual resist molecule in the initial film is identical, and so development should be very uniform. The high sensitivity implies that there is very little photoacid actually generated at the imaging doses for this material, and thus the driving force for photoacid diffusion at the line edge is lower. The photoacid counterion in this system is also quite bulky and should help to limit photoacid diffusion. The cross-linking reaction can occur without the movement of the proton, meaning that the solubility switching is not dependent on the photoacid diffusing to each individual reaction site.

IV. CONCLUSIONS

Five different molecular glass CARs were investigated based on a common molecular resist core. THPE-THP was found to form insoluble residues after exposure, and so was not tested in e-beam for high resolution imaging. THPE-EE was an oil at room temperature, but the EE protecting group could possibly work as a low activation energy protecting group on larger molecular resist cores. THPE-tBoc imaged with reasonable contrast and could be processed under similar conditions as tBoc-PHOST, but the fully protected glass required high levels of photoacid to cause deprotection which resulted in photoacid diffusion induced pattern blur. Although this specific resist could not resolve sub-100 nm images due to photoacid diffusion induced blur, it appeared that it could be optimized and redesigned for improved imaging. However, sub-50 nm imaging for the THPE-tBoc material is doubtful at any reasonable sensitivity. The THPE-tBoc material did, however, show that the tBoc protecting group does not increase the flexibility of even small core molecules to the point where the glass transition or melting point is lowered to levels where the behavior of the compound suffers. THPE-CL had good sensitivity, but suffered because of the high temperatures required for imaging which led to blurred images. Even though the use of base quencher and diffusion control could likely improve resolution, the high temperatures required for imaging likely would severely limit the ultimate resolution of this material. THPM-Ep had good sensitivity with reasonable contrast and produced excellent high resolution patterns with a low LER (3σ) of 2.3 nm. Its basic imaging shows that it is a good candidate for further study for the 32 nm node and below; indeed, it has already shown the capability to resolve 30 nm lines at 1:3 line/spacing. Its industrial application in semiconductor processing may be limited though due to both the limited choice of PAGs that work with this material (i.e., sulfonic acid PAGs cannot be used and instead this material required non-nucleophilic PAGs such as triphenyl sulphonium hexafluoroantimonate) and the requirement that organic solvents be used for development. However, because of its excellent imaging with high sensitivity at 100 keV, THPM-Ep should receive further consideration as a resist for future high resolution e-beam lithography applications including mask making.

ACKNOWLEDGMENTS

The authors acknowledge Intel Corporation for funding this research and AZ Electronic Materials for the donation of the developers used in this work. The authors would also like to gratefully acknowledge helpful discussions from our collaborator Jeanette Roberts at Intel. Tyler Osborn also is acknowledged for help in gathering SEM images.

[1] D. Yang, S. W. Chang, and C. K. Ober, J. Mater. Chem. **16**, 1693 (2006).
[2] K. Young-Gil, J. Kim, T. Fujigaya, Y. Shibasaki, and M. Ueda, J. Mater. Chem. **12**, 53 (2002).
[3] T. Kadota, H. Kageyama, F. Wakaya, K. Gamo, and Y. Shirota, Chem. Lett. **33**, 706 (2004).
[4] S. W. Chang *et al.*, Proc. SPIE **5753**, 1 (2005).
[5] S. W. Chang, R. Ayothi, D. Bratton, D. Yang, N. Felix, H. B. Cao, H. Deng, and C. K. Ober, J. Mater. Chem. **16**, 1470 (2006).
[6] K. Kojima, T. Hattori, H. Fukuda, T. Hirayama, D. Shiono, H. Hada, and J. Onodera, Proc. SPIE **6153**, 61530G (2006).
[7] D. C. Tully, A. R. Trimble, and J. M. J. Frechet, Adv. Mater. (Weinheim, Ger.) **12**, 1118 (2000).
[8] R. Ayothi, S. W. Chang, N. Felix, H. B. Cao, H. Deng, W. Yueh, and C. K. Ober, J. Photopolym. Sci. Technol. **19**, 1515 (2006).
[9] T. Hirayama *et al.*, Proc. SPIE **5753**, 738 (2005).
[10] D. Shiono, H. Hada, H. Yukawa, H. Oizumi, I. Nishiyama, K. Kojima, and H. Fukuda, Proc. SPIE **6519**, 65193U (2007).
[11] T. Oh, R. Ganesan, J. Yoon, and J. Kim, Proc. SPIE **6153**, 61532G (2006).
[12] J. Y. Dai, S. W. Chang, A. Hamad, D. Yang, N. Felix, and C. K. Ober, Chem. Mater. **18**, 3404 (2006).
[13] Q. Lin, A. D. Katnani, and C. G. Willson, Proc. SPIE **3049**, 974 (1997).
[14] R. A. Lawson, C. Lee, R. Whetsell, W. Yueh, J. Roberts, L. Tolbert, and C. L. Henderson, Proc. SPIE **6519**, 65191N (2007).
[15] A. W. Grant, Q. H. Hu, and B. Kasemo, Nanotechnology **15**, 1175 (2004).
[16] T. Sakamizu, H. Shiraishi, H. Yamaguchi, T. Ueno, and N. Hayashi, Jpn. J. Appl. Phys., Part 1 **31**, 4288 (1992).
[17] R. Schwalm, H. Binder, and D. Funhoff, J. Appl. Polym. Sci. **78**, 208 (2000).
[18] C. H. Park, S. Takahara, and T. Yamaoka, Polym. Adv. Technol. **17**, 156 (2006).
[19] A. R. Pawloski, A. Acheta, I. Lalovic, B. M. La Fontaine, and H. J. Levinson, Proc. SPIE **5376**, 414 (2004).